60 Rec'd PCT/PTO 10 JAN 2001

FORM PTO-1390 (Modified) (REV 11-98) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: **201034US0PCT**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR: 09/720262

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP00/01600	**16 March 2000**	**18 March 1999(earliest)**

TITLE OF INVENTION
CATALYSTS FOR WATER GAS SHIFT REACTION, METHOD FOR REMOVING CARBON MONOXIDE IN HYDROGEN GAS AND FUEL CELL GENERATION SYSTEM

APPLICANT(S) FOR DO/EO/US
Akira IGARASHI, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   - b. ☒ has been transmitted by the International Bureau.
   - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   - b. ☐ have been transmitted by the International Bureau.
   - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report
Notice of Priority
PCT/IB/304
PCT/IB/308
Drawings (7 Sheets)

JC07 Rec'd PCT/PTO 10 JAN 2001

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/720262	INTERNATIONAL APPLICATION NO. PCT/JP00/01600	ATTORNEY'S DOCKET NUMBER 201034US0PCT

21. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

	CALCULATIONS	PTO USE ONLY
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1,000.00**		
☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but Internation Search Report prepared by the EPO or JPO **$860.00**		
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**		
☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**		
☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	**$860.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$130.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	25 - 20 =	5	x $18.00	**$90.00**	
Independent claims	3 - 3 =	0	x $80.00	**$0.00**	
Multiple Dependent Claims **(check if applicable).**			☐	**$0.00**	
	TOTAL OF ABOVE CALCULATIONS =			**$1,080.00**	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) **(check if applicable).**			☐	**$0.00**	
	SUBTOTAL =			**$1,080.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +				**$0.00**	
	TOTAL NATIONAL FEE =			**$1,080.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).**			☐	**$0.00**	
	TOTAL FEES ENCLOSED =			**$1,080.00**	
				Amount to be: refunded	$
				charged	$

☒ A check in the amount of **$1,080.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. in the amount of to cover the above fees. A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

NEUSTADT, P.C.

22850

Surinder Sachar
Registration No. 34,423

Surinder Sachar

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

1-10-01

DATE

DOCKET NO. 201034US0PCT

IN RE APPLICATION OF: Akira IGARASHI, et al.

SERIAL NO.: New U.S. PCT Application (Based on PCT/JP00/01600)

FILED: HEREWITH

FOR: CATALYSTS FOR WATER GAS SHIFT REACTION, METHOD FOR REMOVING CARBON MONOXIDE IN HYDROGEN GAS AND FUEL CELL GENERATION SYSTEM

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

Sir:

Transmitted herewith is an amendment in the above-identified application.

☒ No additional fee is required.

☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement previously submitted.

☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement submitted herewith.

☒ Additional documents filed herewith: PCT Transmittal Letter/Notice of Priority/Drawings (7 Sheets) English Translation of Specification/Request for Consideration/PCT/IB/304/Preliminary Amendment/PCT/IB/308 International Search Report/Check for $1,080.00

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	(Col. 1)		(Col. 2)	(Col. 3)	SMALL ENTITY		OTHER THAN A SMALL ENTITY	
	CLAIMS REMAINING AFTER		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
TOTAL	* 25	MINUS	** 25	= 0	X9 =	$	X18 =	$ .00
INDEP	* 3	MINUS	*** 3	= 0	X40 =	$	X80 =	$ .00
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM					+135=	$	+270=	$
					TOTAL	$	TOTAL	$ .00

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*If the entry in Column 2 is less than the entry in Column 1 write "0" in Column 3.
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***If the "Highest Number Previously paid for" IN THIS SPACE is less than 3 write "3" in this space.

DOCKET NO. 201034US0PCT

IN RE APPLICATION OF: Akira IGARASHI, et al.

SERIAL NO.: New U.S. PCT Application (Based on PCT/JP00/01600)

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ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

Sir:

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	(Col. 1)		(Col. 2)	(Col. 3)	SMALL ENTITY		OTHER THAN A SMALL ENTITY	
	CLAIMS REMAINING AFTER		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
TOTAL	* 25	MINUS	** 25	= 0	X9 =	$	X18 =	$ .00
INDEP	* 3	MINUS	*** 3	= 0	X40 =	$	X80 =	$ .00
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM					+135=	$	+270=	$
					TOTAL	$	TOTAL	$ .00

__ A check in the amount of $____________ is attached.

XX Please charge any additional fees for the papers being filed herewith and for which no check is enclosed herewith, or credit any overpayment to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

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09/720262

201034US0 PCT 10 JAN 2001

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :

AKIRA IGARASHI ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: NEW PCT APPLICATION :
(BASED ON PCT/JP00/01600)

FILED: HEREWITH :

FOR: CATALYSTS FOR WATER GAS SHIFT REACTION, METHOD FOR REMOVING CARBON MONOXIDE IN HYDROGEN GAS AND FUEL CELL GENERATION SYSTEM

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as follows:

Claim 3, line 2, delete "or 2".

Claim 4, line 2, change "any one of claims 1 to 3" to --claim 1--.

Claim 6, line 2, change "any one of claims 1 to 5" to --claim 1--.

Claim 8, line 2, change "any one of claims 1 to 7" to --claim 1--.

--10. (Amended) The method for removing carbon monoxide according to claim 9 characterized in that the metal oxide carrier is selected from the group consisting of zirconia, alumina, titania, silica, silica-magnesia, zeolite, magnesia, niobium oxide, zinc oxide and chromium oxide [the catalyst for the water shift reaction according to any one of claims 1 to 8 is used].

--12. (Amended) The fuel cell generation system according to claim 11 wherein the metal oxide is at least one metal oxide selected from the group consisting of zirconia, alumina, titania, silica, silica-magnesia, zeolite, magnesia, niobium oxide, zinc oxide and chromium oxide [catalyst for the water gas shift reaction according to any one of claims 1 to 8 is used].--

Please add the following claims:

--13. The method for removing carbon monoxide according to Claim 9, wherein the supported platinum is in an amount from 0.1% to 10% by weight based on the weight of the metal oxide carrier.

14. The method for removing carbon monoxide according to Claim 9, wherein the catalyst further comprise rhenium supported on the metal oxide carrier.

15. The method for removing carbon monoxide according to Claim 14, wherein wherein the supported rhenium is in an amount from 0.1 % to 10 % by weight based on the metal oxide carrier.

16. The method for removing carbon monoxide according to Claim 9, wherein the catalyst further comprises at least one metal selected from the group consisting of yttrium, calcium, chromium, samarium, cerium, tungsten, neodymium, praseodymium, magnesium, molybdenum and lanthanum supported on the metal oxide carrier.

17. The method for removing carbon monoxide according to claim 16, wherein the supported metal is in an amount from 0.1 % to 10 % by weight based on the weight of the metal oxide carrier.

18. The method for removing carbon monoxide according to claim 9, wherein the catalyst has been subjected to hot water treatment

19. The fuel cell generation system according to claim 11, wherein the supported platinum is in an amount from 0.1% to 10% by weight based on the weight of the metal oxide carrier.

20. The fuel cell generation system according to claim 11, wherein the catalyst further comprise rhenium supported on the metal oxide carrier.

21. The fuel cell generation system according to claim 20, wherein the supported rhenium is in an amount from 0.1 % to 10 % by weight based on the metal oxide carrier.

22. The fuel cell generation system according to claim 11, wherein the catalyst further comprises at least one metal selected from the group consisting of yttrium, calcium, chromium, samarium, cerium, tungsten, neodymium, praseodymium, magnesium, molybdenum and lanthanum supported on the metal oxide carrier.

23. The fuel cell generation system according to claim 22, wherein the supported metal is in an amount from 0.1 % to 10 % by weight based on the weight of the metal oxide carrier.

24. The fuel cell generation system according to claim 11, wherein the catalyst has been subjected to hot water treatment.

25. The catalyst for the water gas shift reaction according to claim 4, wherein the catalyst further comprises at least one metal selected from the group consisting of yttrium,

calcium, chromium, samarium, cerium, tungsten, neodymium, praseodymium, magnesium, molybdenum and lanthanum supported on the metal oxide carrier.--

REMARKS

Claims 1-25 are active in the present application. The claims are amended to remove multiple dependencies. Claims 13-25 are supported by Claims 1-12 and the specification as filed herewith. No new matter is added. An action on the merits and allowance of the claims is solicited.

Respectfully submitted,

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JC07 Rec'd PCT/PTO 10 JAN 2001

DESCRIPTION

CATALYSTS FOR WATER GAS SHIFT REACTION, METHOD FOR REMOVING CARBON MONOXIDE IN HYDROGEN GAS AND FUEL CELL GENERATION SYSTEM

Technical Field

The present invention relates to a water-gas-shift-reaction catalyst used for converting and removing carbon monoxide (CO) in a gas which is rich in hydrogen through a water gas shift reaction, a method for removing carbon monoxide in a hydrogen gas using such catalyst, and a fuel cell generation system using such catalyst.

Background Art

A reformed gas which is rich in hydrogen is produced by a steam reforming reaction of a hydrocarbon gas, liquid or solid, or a fuel such as methanol or the like with steam, and such reformed gas contains carbon monoxide as a by-product. The reformed gas is used for a supply of hydrogen as a fuel in a fuel cell electricity generation system.

It is contemplated that among fuel cells, a polymer electrolyte fuel cell (or solid polymer fuel cell) is used for a vehicle, a compact generator and a domestic co-generation system since it operates at a lower temperature, produces a

higher power density, and is expected to be compact and light and to have a shortened operation period.

The polymer electrolyte fuel cell uses a perfluorosulfonic acid based polymer membrane as a proton conductive solid electrolyte and operates at a temperature between 50 °C and 100 C°. However, since the polymer electrolyte fuel cell operates at such a lower temperature, it is likely to be poisoned by an impurity contained in the reformed gas which is rich in hydrogen. Particularly, platinum used for an electrode in a fuel cell unit is likely to be poisoned by CO, and generation performance of the unit is degraded when CO is contained in the reformed gas beyond a certain predetermined concentration.

Thus, a CO removal unit is provided downstream a reforming unit which produces the reformed gas rich in hydrogen from the fuel, and CO is selectively converted and removed through a water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) so that a concentration of CO in the reformed gas is usually reduced to not greater than 1 %. A catalyst for the water gas shift reaction is used for the CO removal as a CO conversion catalyst, and hitherto a Cu-Zn based catalyst has been conventionally used. It is noted that in the generation system using the polymer electrolyte fuel cell, a selective oxidation reaction unit is additionally provided downstream the CO removal unit so that the CO

concentration in the hydrogen gas is further reduced for example to not larger then 50 ppm, and the hydrogen gas of which CO concentration is thus reduced is supplied to a fuel cell unit.

Disclosure of Invention

However, since an activity of the Cu-Zn based catalyst is low, a large amount of the catalyst has to be used in order that the CO concentration in the hydrogen gas is reduced to not larger than 1 %. Further, its activity ages, and therefore the catalyst has be replaced with a fresh catalyst periodically. Therefore, it is difficult to apply the Cu-Zn based catalyst to a fuel cell generation system wherein start and stop are repeatedly carried out, and in particular to a compact fuel cell generation system.

The present invention has been made considering the problem as described above, and an object of the present invention is to provide a catalyst for a water gas shift reaction which can removes CO effectively in a hydrogen gas preferably within a broader temperature range and which can be used for the removal of CO contained in the hydrogen gas. Such catalyst can be used as a catalyst which accelerates a water gas shift reaction when CO is removed from a gas rich in hydrogen which is formed particularly in a fuel cell generation system.

Another object of the present invention is to provide a method for reducing carbon monoxide in a hydrogen gas in which method the hydrogen gas containing carbon monoxide contacts with the catalyst for the water gas shift reaction catalyst as described above.

A further object of the present invention is to provide a fuel cell generation system characterized in that a hydrogen gas which contains carbon monoxide contacts with the catalyst for the water gas shift reaction, and an obtained hydrogen gas of which carbon monoxide content is reduced is supplied to a fuel cell unit.

In the first aspect, the present invention provides a catalyst for a water gas shift reaction characterized in that at least platinum is supported as an active component on a metal oxide carrier.

In the catalyst according to the present invention, the metal oxide carrier is preferably at least one selected from the group consisting of zirconia, alumina, titania, silica, silica-magnesia, zeolite, magnesia, niobium oxide, zinc oxide and chromium oxide (it is to be noted that a metal herein includes also silicon). Among those oxides, zirconia is particularly preferable. Also, a carrier of zirconia, alumina, silica, silica-magnesia, zeolite, magnesia, niobium oxide, zinc oxide or chromium oxide coated with titania may be used as the metal oxide carrier.

As to the catalyst according to the present invention, an amount of the active component supported by the carrier is preferably between 0.1 % by weight and 10.0 % by weight converted into a platinum metal expression based on a weight of the carrier (that is, based on a weight of the carrier itself which does not include the active component, which is also applicable hereinafter to the amount of the supported active component).

According to one embodiment, rhenium is supported as another active component in addition to platinum in the catalyst of the present invention. In this case, an amount of supported rhenium (converted into a rhenium metal expression) is preferably between 0.1 % by weight and 10.0 % by weight based on a weight of the carrier.

In a further embodiment, at least one other metal selected from the group consisting of yttrium, calcium, chromium, samarium, cerium, tungsten, neodymium, praseodymium, magnesium, molybdenum and lanthanum is further supported as a further active component in the catalyst of the present invention in addition to platinum and rhenium optionally present as described above. In this case, an amount of the further supported active component(s) (converted into a metal expression) is in total preferably between 0.1 % by weight and 10.0 % by weight based on a weight of the carrier.

As to the catalyst according to the present invention, any suitable manner may support the active component on the carrier. For example, a salt of a metal which is suitable for the active component is dissolved in a suitable solvent such as water, and thus obtained solution is mixed with the carrier (for example in a powder form) to produce a mixture (for example a slurry) before the mixture is dried (preferably dried by heating), so that the carrier is obtained as the catalyst for the water gas shift reaction on which carrier the active component is supported.

The obtained catalyst for the water gas shift reaction is preferably subjected to firing thereafter. In the present invention, firing means a treatment wherein the carrier on which the active component is supported is kept at an elevated temperature, and makes it possible to produce a catalyst of which activity is higher. For example, the carrier is kept at a temperature between 400 °C and 600 °C (for example, 500 °C) for a period between one hour and six hours (for example, two hours) in a suitable atmosphere (for example, in air or in an inert atmosphere).

In other embodiment, in place of or before firing, the catalyst for the water gas shift reaction which is produced by the above supporting is preferably subjected to a washing treatment. The washing treatment is carried out using water, preferably warm water and more preferably hot

water (for example, boiling water). Concretely, the washing treatment is so carried out that the carrier which includes the active component thereon is dispersed in water which is agitated, and then the carrier is separated (for example, by filtration) followed by drying.

In the second aspect, the present invention provides a process of producing a catalyst for a water gas shift reaction which removes carbon monoxide in a hydrogen gas, which process comprises the steps of:

(1) producing a slurry by mixing a metal oxide carrier and a solution (preferably an aqueous solution) of a platinum salt, and

(2) drying thus obtained slurry so as to obtain a dried carrier. According to this process, the catalyst for the water gas shift reaction according to the present invention as described above is produced.

The process according to the present invention may further comprise the step of (3) firing the dried carrier thus obtained. In another embodiment, in place of or before carrying out the firing step, the process may further comprise the step of (4) washing the obtained dried carrier or the fired carrier and particularly washing it with hot water. It is noted that in the process according to the present invention, the platinum salt is converted to platinum as the active component and supported during

drying the slurry drying (step (2)), and further during the firing (step (3)) and/or during the washing (step (4)).

The explanations as to the catalyst of the present invention as described above are applicable to the metal oxide carrier, the amount of the supported platinum, the firing, and the washing and so on in the process of producing the catalyst according to the present invention. In addition, rhenium in addition to platinum may be supported by the carrier, in which a solution of a rhenium salt is used in place of the solution of the platinum salt.

As to supporting rhenium, rhenium together with platinum may be supported by the carrier, in which an aqueous solution containing both the rhenium salt and the platinum salt together is prepared (or an aqueous solution containing the platinum salt and an aqueous solution containing the rhenium salt are mixed), and the steps described above are carried out using the obtained solution (or the mixture). Alternatively, the above steps (1) and (2) in series are repeated twice wherein one component is supported first and the other component is supported subsequently so that the carrier is obtained which supports platinum and rhenium.

In the process according to the present invention, in addition to platinum or in addition to platinum and rhenium as the additional active component, at least one other metal

as described above may be supported by the carrier as a further additional active component. In this case, all of the metals may be supported together or each of the metals may be supported separately as in the case of rhenium as described above. It is noted that as to amounts of rhenium and the other metal to be supported, the above explanations as to the catalyst of the present invention are applicable.

Further, in the third aspect, the present invention provides a method for removing carbon monoxide from a hydrogen gas containing carbon monoxide characterized in that the hydrogen gas is contacted with a catalyst for a water gas shift reaction which comprises a metal oxide carrier supporting at least platinum. As the catalyst for the water gas shift reaction in this method, the catalyst according to the present invention which is described above can be used.

In this method, the hydrogen gas which contains carbon monoxide is contacted with the catalyst for the water gas shift reaction which is retained by a proper means or manner at a temperature between 200 °C and 400 °C and preferably a temperature between 220 °C and 350 °C in the presence of steam. The steam may be supplied in any suitable manner. The hydrogen gas which is used in this method is not particularly limited as far as it

contains carbon monoxide. For example, the method according to the present invention is preferably applied to a reformed gas which contains hydrogen as a main component, and also contains carbon monoxide and steam so that a concentration of carbon monoxide contained in the gas is reduced.

Thus, in the fourth aspect, the present invention provides a fuel cell generation system which comprises a CO removing unit which contains a catalyst for a water gas shift reaction comprising a metal oxide carrier which supports at least platinum, which system is characterized in that the CO removing unit contacts a reformed gas as a hydrogen gas containing carbon monoxide produced by a steam reforming unit with the catalyst for the water gas shift reaction, whereby the hydrogen gas of which carbon monoxide concentration has been reduced is produced. The hydrogen gas of which carbon monoxide concentration has been reduced is supplied to a fuel cell unit. It is noted that when thus reduced carbon monoxide concentration in the hydrogen gas has to be further reduced before the hydrogen gas is supplied to the fuel cell unit (for example in the case of the polymer electrolyte fuel cell generation system), the hydrogen gas of which carbon monoxide concentration has been reduced through the CO removing unit is passed through a selective oxidation unit before it is

supplied to the fuel cell unit.

Brief Description of Drawings

Fig. 1 is a graph which shows relationships between a reaction temperature and a CO conversion when catalysts according to Examples 1 to 5 and Comparative Example were used;

Fig. 2 is a graph which shows relationships between a reaction period and a CO conversion when catalysts according to Examples 3 and 4 and Comparative Example were used;

Fig. 3 is a graph which shows reaction selectivities when catalysts according to Example 3 and Examples 6 to 16 were used.

Fig. 4 is a graph which shows relationships between a reaction temperature and a CO conversion when catalysts according to Examples 3, 17 and 18 and Comparative Example were used;

Fig. 5 is a graph which shows relationships between a reaction period and a CO conversion when catalysts according to Example 3, 4 and 19 and Comparative Example were used;

Fig. 6 is a graph which shows CO conversions when catalysts according to Examples 3 and 20 to 27 and Comparative Example were used;

Fig. 7 is a graph shows relationships between a reaction temperature and a CO conversion when catalysts according to Example 17 and Comparative Example were used in Example 28.

Embodiment for Carrying Out the Invention

Embodiments according to the present invention will be explained hereinafter.

In the present invention, as the metal oxide which is the carrier for the active component, at least one selected from the group consisting of zirconia, alumina, silica, silica-magnesia, zeolite, magnesia, niobium oxide, zinc oxide, chromium oxide and these metal oxide coated with titania (for example those coated through CVD), and titania. Those metal oxides may be ones commercially available. The carrier may be in the form of powder or particles, or in the form of a shaped article such as a pellet.

Alternatively, the metal oxide as described above may be one which are produced from other compound(s) by any suitable method. For example, zirconia as the carrier may be prepared by firing a hydrate of zirconium hydroxide as a starting material.

Having platinum as the active component supported on such a carrier (for example a zirconia carrier) may be performed by adding the carrier into an aqueous solution of

a platinum salt (for example chloroplatinic acid), evaporating the solution while stirring, and optionally further heating the material obtained through evaporating so as to dry it, whereby the catalyst for the water gas shift reaction according to the present invention is obtained. Optionally, when the material obtained through evaporating or further heating has a large size (for example when it is in the form of a mass, it may be pulverized. When necessary, the carrier supporting the active component may be subjected to the firing treatment optionally after the pulverization.

It is noted that when the obtained carrier is fine, it may be pressed to produce pellets using for example a press followed by pulverizing the produced pellets so as to produce catalyst particles having a diameter between 0.5 mm and 1.0 mm. Such carrier may be used as the catalyst for the water gas shift reaction wherein the active component is supported by the carrier, and CO contained in the hydrogen gas is removed using the particles.

As to the catalyst for the water gas shift reaction according to the present invention, a supported amount of platinum is in the range between 0.1 % and 10 % by weight based on the carrier weight. When the supported amount of platinum is less than 0.1 % by weight, it is difficult to have a sufficient catalyst activity to convert CO in H_2 to CO_2

through the water gas shift reaction upon the removal of CO. When the supported amount of platinum is greater than 10.0 % by weight, the catalyst activity is not so further improved and a production cost of the catalyst often becomes unprofitable.

The CO removing catalyst may be also obtained by having other active component supported on the carrier in addition to platinum. As such other active component, rhenium and yttrium, calcium, chromium, samarium, cerium, tungsten, neodymium, praseodymium, magnesium, molybdenum and lanthanum may be used. One or more metals selected from these metals may be supported on a zirconia carrier. When other active component(s) is supported, a salt of the selected active component is used in the supporting manner as described in the above.

Upon the preparation of the catalyst for the water gas shift reaction wherein the active component(s) in addition to platinum is supported on the carrier, when a metal(s) such as rhenium, and/or yttrium, calcium, chromium, samarium, cerium, tungsten, neodymium, praseodymium, magnesium, molybdenum and/or lanthanum is used as the active component, an aqueous solution of a platinum salt (such as chloroplatinic acid) and an aqueous solution(s) of a salt(s) of said other metal(s) (or an aqueous solution which contains these all salts together) are mixed with the

carrier, and then the obtained mixture is evaporated while being stirred, and the material obtained through the evaporation is heated so as to further dry if necessary. A subsequent treatment thereafter may be similar to that in the case of having platinum supported as described before. When a plurality of the metals are supported on the carrier as described above, it is not particularly critical in which form the metals are supported on the carrier as long as the effect as to the water gas shift reaction is provided. Thus, the metals may be or may not be in a state of an alloy.

By having at least one selected from the above metals in addition to platinum supported on the carrier, the catalyst activity to remove CO is increased, and hydrogen consumption is because of methanation reaction simultaneously prevented. The methanation reaction in which CO reacts with H_2 to form methane occurs as a side reaction upon the conversion of CO in H_2 into CO_2 for the purpose of the removal of CO. Particularly, by having rhenium in addition to platinum supported, an effect to further increase the catalyst activity to remove CO is obtained.

In this case, a supported amount of rhenium is preferably in the range between 0.1 % and 10.0 % by weight converted into the rhenium metal expression based on the carrier weight. As to the metal(s) other than

rhenium, a supported amount of such metal(s) is preferably in the range between 0.1 % and 10.0 % by weight of the total of such metal(s). When the supported amount of such metal(s) is less than 0.1 % by weight, it is difficult to have a sufficient effect to prevent the methanation reaction. When the supported amount of such metal(s) is greater than 10.0 % by weight, the effect to prevent the methanation reaction is not so further improved and a production cost of the catalyst becomes unprofitable.

In the above description, the active component such as platinum is supported by adding the aqueous solution of the salt of the active component to the carrier followed by evaporating the solution, further heating to dry and then firing the carrier. However, the catalyst for the water gas shift reaction according to the present invention may be produced by washing and particularly washing with hot water the carrier after evaporating or further heating. That is, the catalyst comprising the carrier supporting platinum and optionally the other metal(s) is stirred in the hot water (at a temperature between 80 °C and 100 °C, preferably boiling water) for a predetermined period (for example one hour) followed by filtration so as to separate the catalyst. After repeating such washing several times (and preferably until filtrate gets clear) and then drying, a catalyst is produced. Alternatively, the dried catalyst may be pressed

into the form of pellets, and thus obtained pellets may be pulverized into particles having a diameter between 0.5 mm and 1.0 mm so that the catalyst for the water gas shift reaction wherein the carrier supports platinum is obtained. When washing, and particularly washing with the hot water is carried out as described above, the subsequent firing may be or may not be carried out.

By carrying out washing as described above, it is contemplated that what is present in the carrier and able to adversely affect the CO removal through the water gas shift reaction (for example, a material which is resulted from the carrier or the active component salt such as a chlorine ion) is reduced or removed from the carrier so that the catalyst activity to remove CO is further increased. For example, the adverse effect induces conversion degradation, selectivity degradation and increase of a by-product(s).

It is generally noted that when the water gas shift reaction is conducted while using the catalyst according to the present invention, the catalyst is preferably subjected to a reduction treatment prior to conducting the water gas shift reaction since the active metal may have been oxidized. The reduction treatment may be carried out in any suitable manner, and for example in a manner wherein the catalyst is contacted with hydrogen at an elevated temperature.

According to the present invention, the catalyst for the water gas shift reaction produced as described in the above is able to be used in a water gas shift reaction unit wherein CO is removed from a reformed gas which is rich in hydrogen and which is produced from a hydrocarbon based gas (such as a butane gas), a hydrocarbon liquid or solid, or an alcohol fuel such as methanol and steam through a steam reforming reaction unit. Such water gas shift reaction unit is combined with a selective oxidization unit (for example a unit comprising a Ru-based selective oxidation catalyst) which is located downstream the unit, so that the CO concentration of the reformed gas is reduced below a predetermined level, and such reformed gas is supplied to a fuel cell unit, whereby a fuel cell generation system for example, the polymer electrolyte fuel cell generation system is formed. Such system is optimal for an automobile, a compact generator or a domestic cogeneration system.

Industrial Applicability

The catalyst for the water gas shift reaction according to the present invention wherein the metal oxide carrier supports at least platinum is able to effectively remove CO in a hydrogen gas at a temperature within a broader temperature range for example between 200 °C and 400 °C

so that it is easily applied to a compact and portable fuel cell generation system which repeats its start and stop operations.

When the metal oxide carrier is at least one selected from the group consisting of zirconia, alumina, silica, silica-magnesia, zeolite, magnesia, niobium oxide, zinc oxide and chromium oxide and these metal oxide coated with titania, and titania, the CO removing activity of the catalyst for the water gas shift reaction in which platinum is supported is effectively obtained. Among them, using zirconia as the carrier is in particular effective. In addition, when the supported amount of platinum is in the range between 0.1 % by weight and 10 % by weight based on the carrier weight, the CO removing activity from the reformed gas of the catalyst becomes further more effective.

The catalyst in which rhenium in addition to platinum is supported is able to enhance the CO removing activity of the catalyst and simultaneously to prevent the occurrence of the methanation reaction. In addition, when the supported amount of rhenium is in the range between 0.1 % by weight and 10 % by weight based on the carrier weight, the effect to prevent the methanation reaction is effectively achieved.

When the carrier supports, in addition to platinum or in addition to platinum and rhenium, at least one metal

selected from the group consisting of yttrium, calcium, chromium, samarium, cerium, tungsten, neodymium, praseodymium, magnesium, molybdenum and lanthanum, it is possible to enhance the CO removing activity and simultaneously to prevent the occurrence of the methanation reaction. In addition, when the supported amount of those metals is in the range between 0.1 % by weight and 10 % by weight based on the carrier weight, the effect to prevent the methanation reaction is effectively achieved.

It is noted that the catalyst which is obtained by the washing treatment and particularly the washing treatment using the hot water after the active component has been supported has the enhanced activity, so that such catalyst is preferably used for the removal of CO from the hydrogen gas.

In addition, the reformed gas rich in hydrogen which is produced through the steam reforming reaction of a butane gas as a hydrocarbon based fuel with steam may be contacted with the catalyst for the water gas shift reaction according to the present invention, followed by being contacted with the Ru-based selective oxidation catalyst, so that thus obtained reformed gas may be supplied to the polymer electrolyte fuel cell, whereby using the reformed gas which is obtained from the fuel through the steam

reforming reaction, through the water gas shift reaction and through the selective oxidation, electrically generation can be carried out by means of the fuel cell.

Examples

The present invention will be concretely explained with reference to examples.

Examples 1 to 5

Using a firing furnace, n-hydrate of zirconium hydroxide ($ZrO_2 \cdot H_2O$, manufactured by Mitsuwa Chemicals Co. Ltd.) was subjected to a firing treatment wherein it was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min., and kept at that temperature for one hour, and thereby zirconium oxide was obtained as a zirconia carrier.

A predetermined amount of the obtained zirconia carrier was charged into an evaporating dish located above a water bath. Pure water was added to the carrier and they are mixed intimately. An aqueous solution of chloroplatinic acid hexahydrate (manufactured by NACALAI TESQE INC.) was added to the evaporating dish, and pure water was further added to reach a predetermined concentration. The dish was located above the water bath while stirring so that the evaporation to dryness of the contents in the dish was

carried out, during which a metal salt depositing on a wall of the evaporating dish was washed away with pure water into the bottom of the dish. Such depositing salt arose with the water evaporation. The evaporation to dryness took one hour.

The obtained material through the evaporation to dryness was further dried at a temperature of about 100 °C for at least 15 hours. The dried material was pulverized into powder in an agate mortar, and the powder was subjected to a firing treatment using a firing furnace wherein it was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min., and kept at that temperature for one hour.

Then, thus obtained powder was pressed at a pressure of about 3600 kg/cm^2 for 10 seconds using a manually operated press, and obtained pellets were pulverized into particles of which diameter was in the range between 0.5 mm and 1.0 mm, whereby a catalyst for the water gas shift reaction was obtained which supported platinum of 3 % by weight (based on the carrier weight) on the zirconia carrier.

It is noted that by variously changing a charged amount of the aqueous solution of chloroplatinic acid, catalysts for the water gas shift reaction (Pt/ZrO_2 catalysts) were produced of which supported amounts of platinum are different as shown in Table 1 below:

Table 1

	supported amount of platinum
Example 1	0.5 % by weight
Example 2	1.0 % by weight
Example 3	3.0 % by weight
Example 4	5.0 % by weight
Example 5	8.0 % by weight

As to the above catalysts according to Examples 1 to 5, their performances to remove CO were estimated as follows:

The catalyst (0.7 ml) was charged into a reaction tube, which was heated to a temperature of 500 °C in one hour and kept at that temperature for one hour while flowing hydrogen through the tube, so that a reduction treatment of the catalyst was carried out. Then, the temperature was lowered to 200 °C in one hour while flowing helium followed by stopping the flow of helium, and a CO containing gas in which H_2O and CO was mixed in a molar ratio (H_2O/CO) of 1.3 was supplied to the tube at a condition of 3650 (1/hr) SV (space velocity) based on CO so that the water gas shift reaction was performed at a temperature of 200 °C, whereby a CO removing experiment was initiated.

After the reaction got stable, gas samples were obtained at an inlet and an outlet of the tube, and analyzed

by means of a gas chromatography (thermal conductivity detector) so that a conversion ratio of CO into CO_2 (CO conversion) was obtained. Further, the reaction temperature was elevated to 250 °C, 300 °C and 350 °C. Similarly to the above, samples were obtained after the reactions became stable, and analyzed whereby obtaining the CO conversions.

It is noted that a CO removing experiment as Comparative Example was also carried out similarly to Examples 1 to 5 except that a Cu/ZnO catalyst ("N211" manufactured by Nikki Chemical Co., Ltd.) was used and the reduction treatment was carried out at a temperature of 300 °C. The results are shown in Fig. 1.

Next, aging of the catalysts was measured. This measurement was carried out as to the catalysts according to Examples 3 and 4 and Comparative Example. After carrying out the reduction treatment first as described above, the temperature of the reaction tube was lowered to 250 °C in one hour followed by stopping the helium supply, and the CO containing gas was supplied as in the above. After the reaction got stable, gas samples were obtained at the inlet and the outlet of the tube every 30 minutes, and analyzed by means of a gas chromatography so that CO conversions were obtained. The results are shown in Fig. 2.

It is seen from Fig. 1 that there is not so large

difference in the catalysts between the Examples and Comparative Example at a temperature of 200 °C, but the Pt/ZrO_2 catalyst of each Example (especially the catalyst having a larger supported amount) has a larger activity than the Cu/ZnO catalyst of Comparative Example. In addition, it is seen from Fig. 2 that the activity of Cu/ZnO catalyst of Comparative Example gradually decreases just after start of the experiment while the activity of Pt/ZrO_2 catalyst of Example 3 or 4 does not decrease.

Therefore, it is contemplated that when considering Figs. 1 and 2, the catalyst according to the present invention has a CO removing performance which is more effective than that of the catalyst of Comparative Example.

Example 6

A predetermined amount of the zirconia carrier which was prepared in Examples 1 to 5 was charged into an evaporating dish located above a water bath. Pure water was added to the carrier and they are mixed intimately. An aqueous solution of chloroplatinic acid hexahydrate (manufactured by NACALAI TESQE INC.) and an aqueous solution of lanthanum nitrate hexahydrate (manufactured by Wako Pure Chemicals Industries, Ltd.) were added to the evaporating dish, and pure water was further added to reach predetermined concentrations. The dish was located

above the water bath while stirring so that the evaporation to dryness of the contents in the dish was carried out, during which metal salts depositing on a wall of the evaporating dish were washed away with pure water into the bottom of the dish. Such depositing salts arose with proceeding of the water evaporation. The evaporation to dryness took one hour.

The obtained material through the evaporation to dryness was further dried at a temperature of about 100 °C for at least 15 hours. The dried material was pulverized into powder in an agate mortar, and the powder was subjected to a firing treatment using a firing furnace wherein it was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min., and kept at that temperature for one hour, so that platinum was supported at in amount of 3.0 % by weight (based on the carrier weight) and lanthanum was supported in an amount of 5.0 % by weight.

Then, thus obtained powder was pressed at a pressure of about 3600 kg/cm^2 for 10 seconds using a manually operated press, and obtained pellets were pulverized into particles of which diameter was in the range between 0.5 mm and 1.0 mm, whereby a catalyst for the water gas shift reaction was obtained which supported platinum and lanthanum on the zirconia carrier.

Examples 7 to 16

Using a salt of a metal which is an active component as shown in Table 2 below in place of lanthanum nitrate hexahydrate, a catalyst for the water gas shift reaction was obtained wherein other metal shown in Table 3 below in addition to platinum was supported by the zirconia carrier.

Table 2

Example	salt of active component	manufacturer
Example 6	lanthanum nitrate hexahydrate	Wako Pure Chemicals
Example 7	praseodymium (III) nitrate hexahydrate	Wako Pure Chemicals
Example 8	yttrium nitrate n-hydrate	Wako Pure Chemicals
Example 9	neodymium (III) nitrate hexahydrate	Wako Pure Chemicals
Example 10	calcium nitrate tetrahydrate	Wako Pure Chemicals
Example 11	samarium nitrate nexahydrate	Wako Pure Chemicals
Example 12	chromium (III) nitrate nonahydrate	NACALAI TESQE
Example 13	cerium (III) nitrate hexahydrate	NACALAI TESQE
Example 14	magnesium nitrate hexahydrate	Wako Pure Chemicals
Example 15	ammonium paratungstate pentahydrate	NACALAI TESQE
Example 16	ammonium molybdate tetrahydrate	Kojund Kenkyusho
Example 17	ammonium perrhenate	Mitsuwa Chemicals

Table 3

	supported amount of Pt (wt %)	other active component	supported amount (wt %)
Example 6	3.0	lanthanum	5.0
Example 7	3.0	praseodymium	5.0
Example 8	3.0	yttrium	5.0
Example 9	3.0	neodymium	5.0
Example 10	3.0	calcium	5.0
Example 11	3.0	samarium	5.0
Example 12	3.0	chromium	5.0
Example 13	3.0	cerium	5.0
Example 14	3.0	magnesium	5.0
Example 15	3.0	tungsten	5.0
Example 16	3.0	molybdenum	5.0
Example 17	3.0	rhenium	1.0
Example 18	3.0	rhenium	3.0

As to the catalysts according to Examples 6 to 16 and Example 3 prepared as described above, the CO removing experiments were carried out similarly to those as described above. The results are shown in Fig. 3. Fig. 3 shows a reaction selectivity which is a ratio of CO converted to CO_2, not to CH_4, upon the CO removal through the conversion of CO to CO_2 at a reaction temperature of 350 °C, and it is seen that the catalysts according to Examples 6 to 16 have higher reaction selectivities than the catalyst according to Example 3 which supports only platinum.

Example 17

A predetermined amount of the zirconia carrier which was prepared in Examples 1 to 5 was charged into an evaporating dish located above a water bath. Pure water was added to the carrier and they are mixed intimately. An aqueous solution of ammonium perrhenate (manufactured by Mitsuwa Chemicals Co. Ltd.) was added to the evaporating dish, and pure water was further added to reach a predetermined concentration. The dish was located above the water bath while stirring so as to dry at a temperature of about 100 °C for at least 15 hours, during which a metal salt depositing on a wall of the evaporating dish were washed away with pure water into the bottom of the dish. Such depositing salt arose with proceeding of the water evaporation. As a result, rhenium was supported by the zirconia carrier.

Then, using the zirconia carrier supporting rhenium, platinum was supported by the carrier similarly to Examples 1 to 5, so that a catalyst for the water gas shift reaction was obtained wherein the zirconia carrier supported 3.0 % by weight of platinum and 1.0 % by weight of rhenium.

Example 18

Similarly to Example 17 except that an added amount

of the aqueous solution of ammonium perrhenate (manufactured by Mitsuwa Chemicals Co. Ltd.) was changed, a catalyst for the water gas shift reaction was obtained wherein the zirconia carrier supported 3.0 % by weight of platinum and 3.0 % by weight of rhenium.

As to the prepared catalysts of Examples 17 and 18 and Example 3 and Comparative Example, the CO removing experiments were carried out similarly to the above. The results are shown in Fig. 4. It is seen from Fig. 4 that the catalysts of Examples 17 and 18 have high activities, and they are highly active even at a temperature equal to or lower than 250 °C.

Example 19

A predetermined amount of the zirconia carrier which was prepared in Examples 1 to 5 was charged into an evaporating dish located above a water bath. An appropriate amount of pure water was added to the carrier and they are mixed intimately. An aqueous solution of chloroplatinic acid (manufactured by NACALAI TESQE INC.) was added to the evaporating dish, and pure water was further added to reach a predetermined concentration. The dish was located above the water bath while stirring so that evaporation to dryness of the contents in the dish was

carried out for one hour, during which a metal salt depositing on a wall of the evaporating dish were washed away with pure water into the bottom of the dish. Such depositing salt arose with proceeding of the water evaporation. The obtained material through the evaporation to dryness was dried dry at a temperature of about 100 °C for at least 15 hours.

The catalyst thus obtained was stirred in hot water (at a temperature of about 100 °C) for about one hour followed by settling and filtrating the catalyst. This process was repeated until the filtrate became clear. Then, the filtrated catalyst was dried at a temperature of 100 °C for at least 15 hours.

Then, thus obtained catalyst was pressed at a pressure of about 3600 kg/cm^2 for about 10 seconds using a manually operated press, and obtained pellets were pulverized into particles of which diameter was in the range between 0.5 mm and 1.0 mm, whereby a catalyst for the water gas shift reaction was obtained which supported platinum of 3.0 % by weight on the zirconia carrier.

As to the prepared catalyst of Examples 19, the same activity aging experiment was carried out similarly to the experiments as to the catalysts of Examples 3 and 4 and Comparative Example. The results are shown in Fig. 5. It

is seen from Fig. 5 that the catalyst of Example 19 has a further higher activity than of course the catalyst of Comparative Example or the catalyst of Example 3 or 4, and that similarly to the catalysts of Examples 3 and 4, the activity of the catalyst of Example 19 does not degrade.

Examples 20 to 27

Using a firing furnace, an agent shown in Table 4 below was subjected to a firing treatment wherein it was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min., and kept at that temperature for one hour, and thereby a carrier of each of Examples 20 to 27 was prepared.

A predetermined amount of the obtained each carrier was charged into an evaporating dish located above a water bath. Pure water was added to the carrier and they are mixed intimately. An aqueous solution of chloroplatinic acid hexahydrate (manufactured by NACALAI TESQE INC.) was added to the evaporating dish, and pure water was further added to reach a predetermined concentration. The dish was located above the water bath while stirring so that the evaporation to dryness of the contents in the dish was carried out, during which a metal salt depositing on a wall of the evaporating dish was washed away with pure water into the bottom of the dish. Such depositing salt arose with

the water evaporation. The evaporation to dryness took two hours.

The obtained material through the evaporation to dryness was further dried at a temperature about 100 °C for at least 15 hours. The dried material was pulverized into powder in an agate mortar, and the powder was subjected to a firing treatment wherein it was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min., and kept at that temperature for one hour.

Then, thus obtained powder was pressed at a pressure of about 3600 kg/cm^2 for 10 seconds using a manually operated press, and obtained pellets were pulverized into particles of which diameter was in the range between 1.4 mm and 2.0 mm, whereby a catalyst for the water gas shift reaction was obtained. The catalyst of each Example supported 3 % by weight of platinum.

Table 4

Example	feedstock for carrier	manufacturer
Example 20	alumina	NACALAI TESQE INC.
Example 21	titania	reference catalyst of Catalysis Society
Example 22	silica	Davison Inc.
Example 23	magnesia	KANTO KAGAKU
Example 24	niobium oxide	NACALAI TESQE INC.

Example 25	zinc oxide	NACALAI TESQE INC.
Example 26	chormium oxide	NACALAI TESQE INC.
Example 27	zeolite	reference catalyst of Catalysis Society

As to the catalysts for the water gas shift reaction of Example 3 and 20 to 27, the CO removal performances were estimated. The estimation experiments were carried out as follows:

First, 3.3 ml of the catalyst for the water gas shift reaction was charged in to a reaction tube, and H_2O and a gas mixture which contained H_2 (70 %), CO (10 %), CO_2 (15 %) and CH_4 (5 %) were supplied to the tube under conditions of a molar ratio (H_2O/CO) of 7.5 and SV (based on the gas mixture) of 5000 (1/hr). The reaction for the CO removal started at a temperature of 250 °C.

After the reaction got stable, a sample was obtained from an outlet of the reaction tube, and analyzed using gas chromatography (thermal conductivity detector and flame ionization detector), whereby the conversion of CO to CO_2 was obtained.

The results are shown in Fig. 6. It is seen from Fig. 6 that the activity of the catalyst of each Example is higher than that of the Cu/ZnO catalyst of Comparative Example.

Example 28

Using the catalyst for the water gas shift reaction according to Example 17, the CO removing performance from a hydrogen gas which contained carbon monoxide was estimated. Experiments for the evaluation were carried out similarly to those as to the catalysts of Examples 20 to 27. It is noted that the similar CO removal experiments were carried out using the Cu/ZnO catalyst as Comparative Example.

The results are shown in Fig. 7. It is seen from Fig. 7 that the CO removal of Example 28 shows a further higher CO removal compared with the Comparative Example.

Example 29

A reformed gas rich in hydrogen which was produced from a butane gas as a hydrocarbon based fuel and steam through the steam reforming reaction was contacted with the catalyst for the water gas shift reaction according to Example 17, and then contacted with an Ru-based selective oxidation catalyst, and thus obtained reformed gas was supplied to a polymer electrolyte fuel cell. An amount of the reformed gas supplied to the fuel cell was 11.6 liters/min. according to an integrating flowmeter, and electricity generation of the fuel cell was estimated using

an electronically loading device (electronic load device).

Generation performance of the fuel cell is shown in the following table:

current	voltage	electric power generation
20 amperes	16.8 volts	336 watts

As seen from the above table, it is confirmed that in the fuel cell system of Example 29 the electricity generation is possible by means of the fuel cell using the reformed gas obtained by the steam reforming reaction of the fuel and through the water gas shift reaction and the selective oxidation reaction.

CLAIMS

1. A catalyst for a water gas shift reaction characterized in that at least platinum is supported on a metal oxide carrier.

2. The catalyst for the water gas shift reaction according to claim 1 characterized in that the metal oxide carrier is at least one selected from the group consisting of zirconia, alumina, titania, silica, silica-magnesia, zeolite, magnesia, niobium oxide, zinc oxide and chromium oxide.

3. The catalyst for the water gas shift reaction according to claim 1 or 2 characterized in that an amount of supported platinum is between 0.1 % by weight and 10.0 % by weight based on a weight of the metal oxide carrier.

4. The catalyst for the water gas shift reaction according to any one of claims 1 to 3 characterized in that rhenium in addition to platinum is further supported on the metal oxide carrier.

5. The catalyst for the water gas shift reaction according to claim 4 characterized in that an amount of supported rhenium is between 0.1 % by weight and 10.0 % by weight based on a weight of the metal oxide carrier.

6. The catalyst for the water gas shift reaction according to any one of claims 1 to 5 characterized in that at least one metal selected from the group consisting of

yttrium, calcium, chromium, samarium, cerium, tungsten, neodymium, praseodymium, magnesium, molybdenum and lanthanum is further supported on the metal oxide carrier in addition to platinum and rhenium which is optionally present.

7. The catalyst for the water gas shift reaction according to claim 6 characterized in that an amount of said supported metal is between 0.1 % by weight and 10.0 % by weight based on a weight of the metal oxide carrier.

8. The catalyst for the water gas shift reaction according to any one of claims 1 to 7 characterized in that the catalyst has been subjected to a hot water treatment after supporting platinum and optional other metal on the metal oxide carrier.

9. A method for removing carbon monoxide in a hydrogen gas characterized in that the hydrogen gas which contains carbon monoxide is contacted with a catalyst for a water gas shift reaction in which catalyst at least platinum is supported on a metal oxide carrier.

10. The method for removing carbon monoxide characterized in that the catalyst for the water gas shift reaction according to any one of claims 1 to 8 is used.

11. A fuel cell generation system characterized in that a hydrogen gas which contains carbon monoxide is contacted with a catalyst for a water gas shift reaction in

which catalyst at least platinum is supported on a metal oxide carrier so as to remove carbon monoxide from the hydrogen gas, which is supplied to a fuel cell.

12. The fuel cell generation system according to claim 11 wherein the catalyst for the water gas shift reaction according to any one of claims 1 to 8 is used.

ABSTRACT

There is provided a catalyst for a water gas shift reaction in a hydrogen gas which is able to effectively remove CO in the hydrogen gas within a broader temperature range.

Such a catalyst for the water gas shift reaction is characterized in that a metal oxide carrier supports at least platinum. The catalyst can be used for removing carbon monoxide in the hydrogen gas. Particularly, such a catalyst can be used in the water gas shift reaction for removing carbon monoxide in a reformed gas in a fuel cell generation system.

Fig. 1

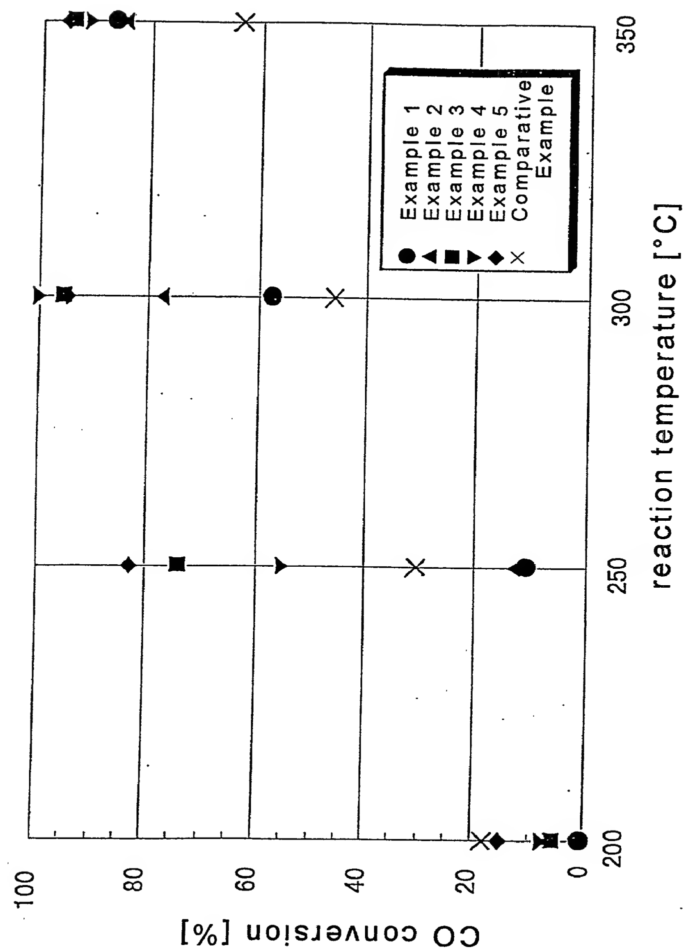

CO conversion [%]
100
80
60
40
20
0
200
250
300
350
reaction temperature [°C]
Example 1
Example 2
Example 3
Example 4
Example 5
Comparative Example

Fig. 2

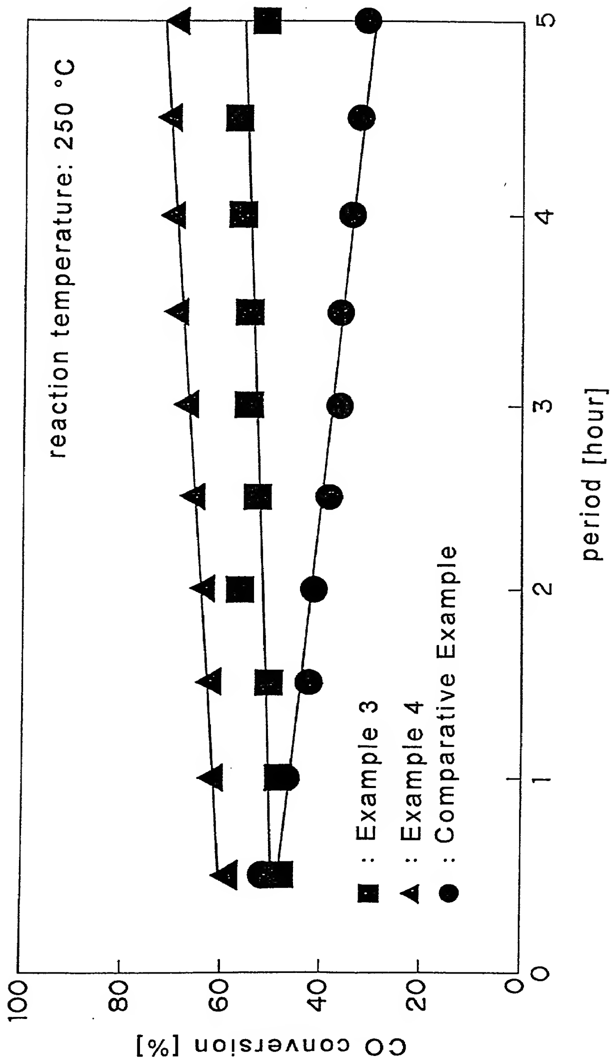

reaction temperature: 250 °C
: Example 3
: Example 4
: Comparative Example
period [hour]
CO conversion [%]
0
1
2
3
4
5
0
20
40
60
80
100

Fig. 3

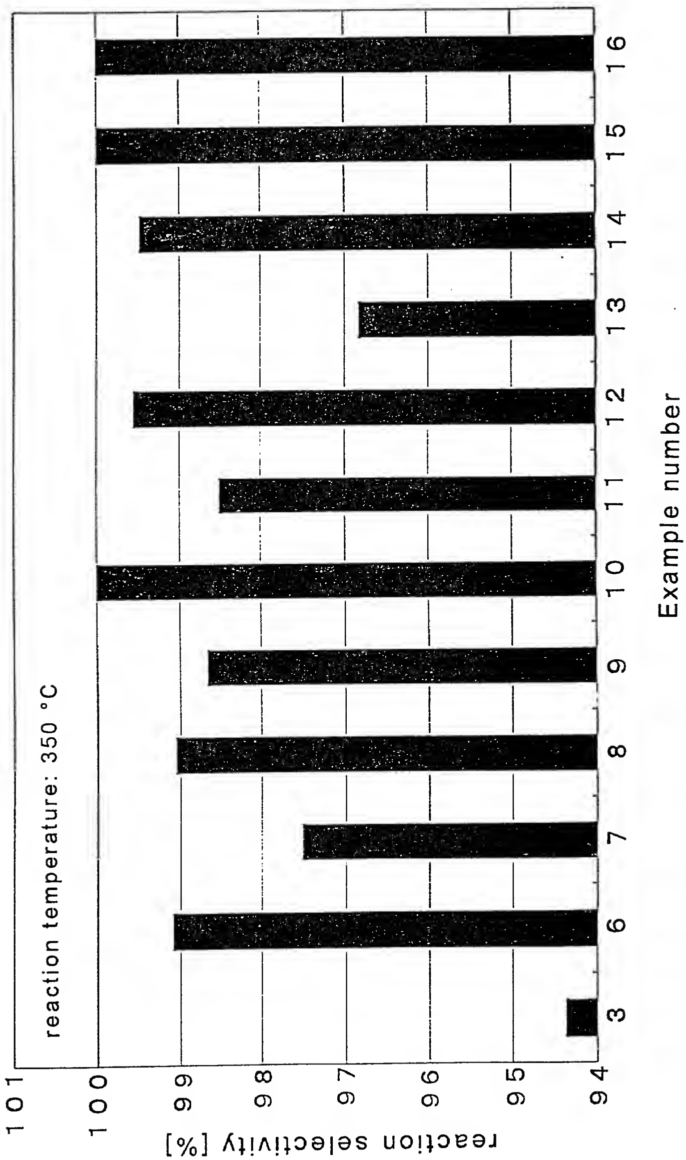

reaction temperature: 350 °C
reaction selectivity [%]
101
100
99
98
97
96
95
94
Example number
3
6
7
8
9
10
11
12
13
14
15
16

Fig. 4

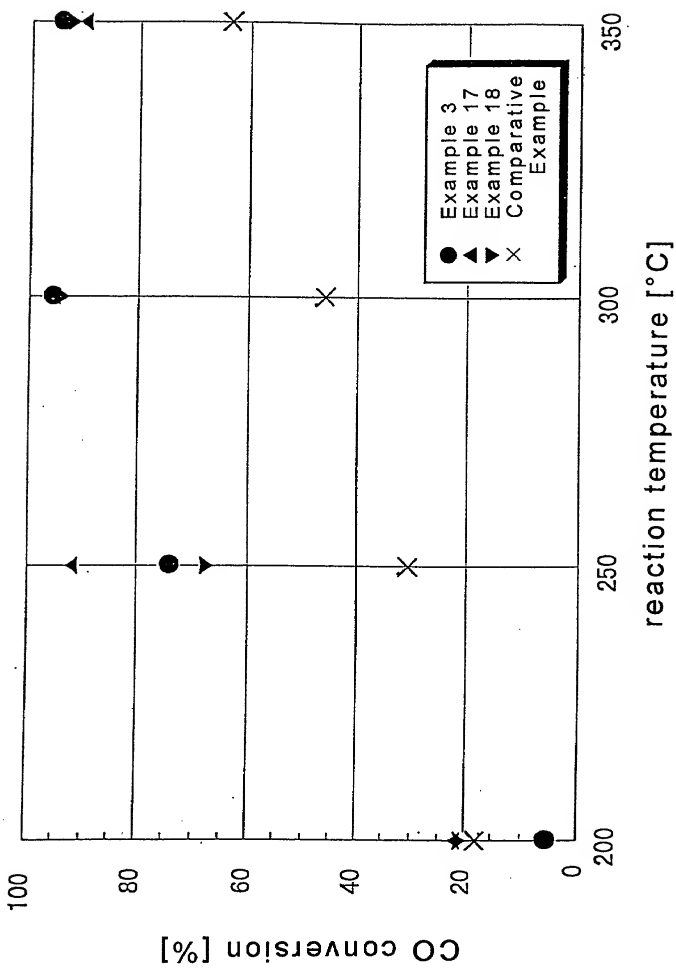
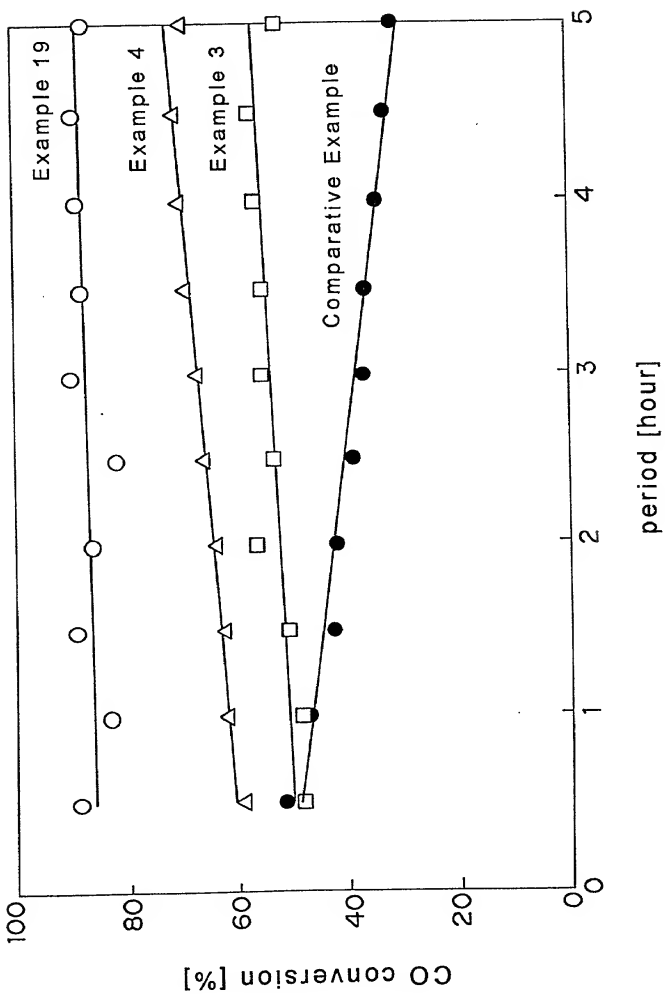

CO conversion [%]
100
80
60
40
20
0
200
250
300
350
reaction temperature [°C]
Example 3
Example 17
Example 18
Comparative Example

Fig. 5


Example 19
Example 4
Example 3
Comparative Example
CO conversion [%]
period [hour]
0
20
40
60
80
100
0
1
2
3
4
5

09/720262

Fig. 6

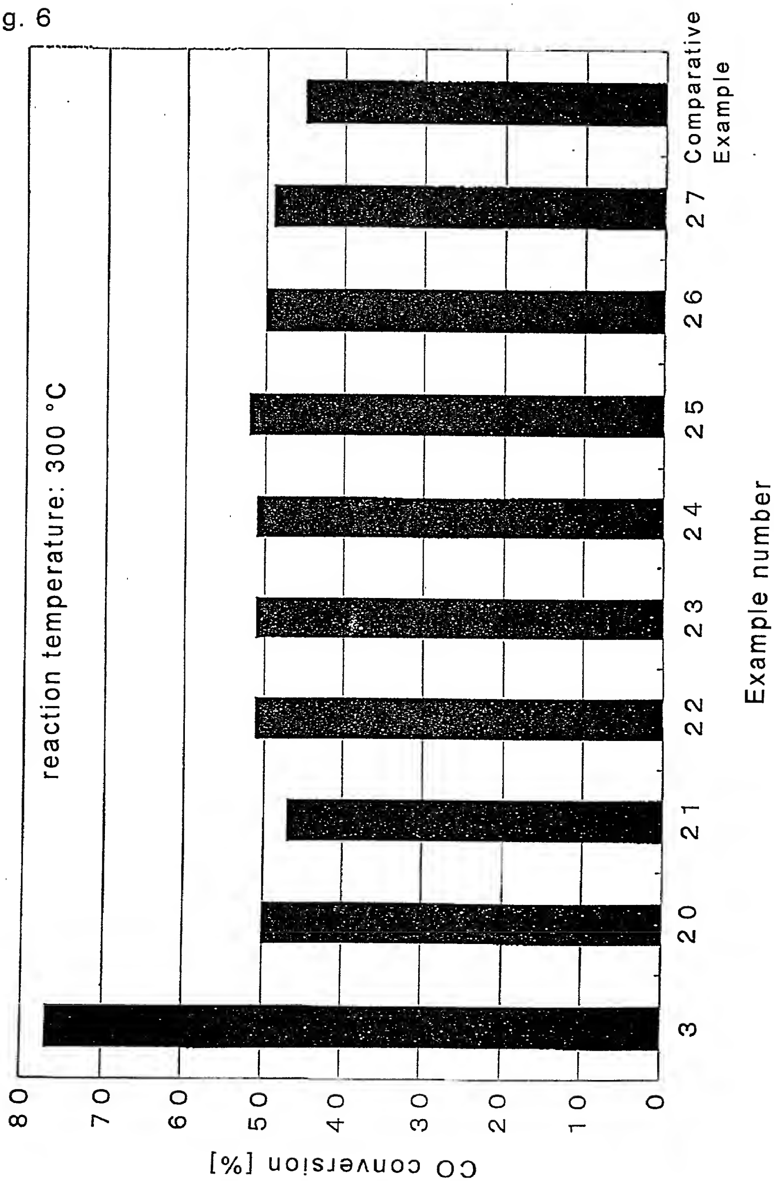
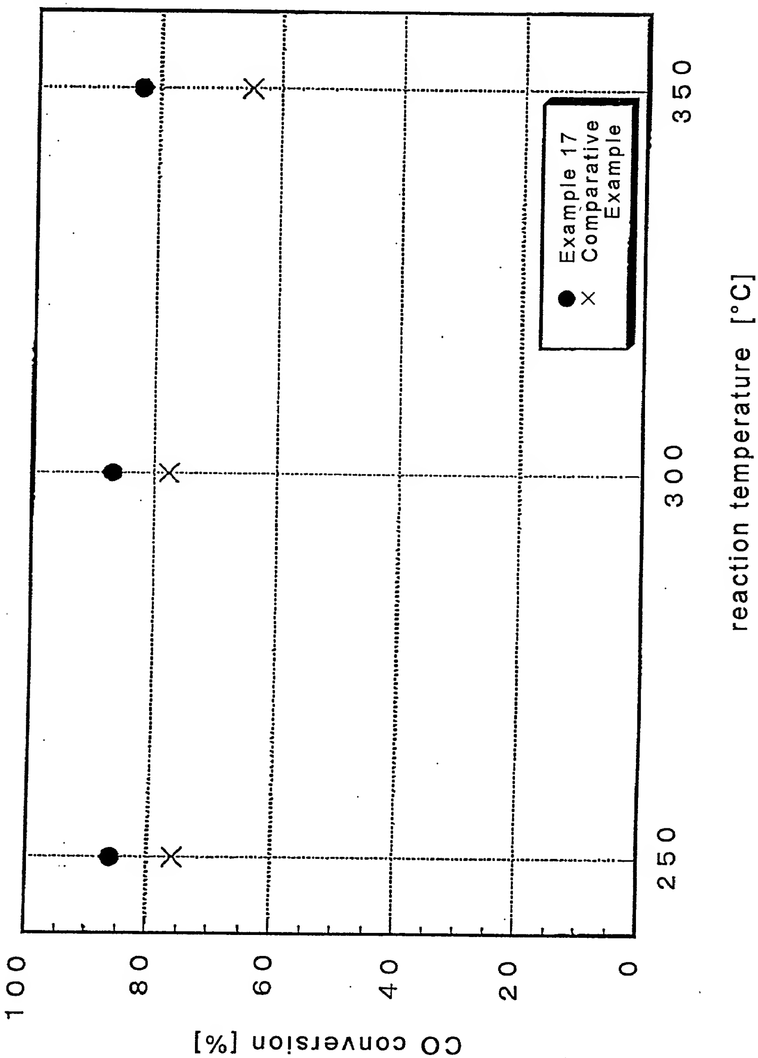


Fig. 7


Example 17
Comparative Example
reaction temperature [°C]
CO conversion [%]
250
300
350
0
20
40
60
80
100

Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

CATALYSTS FOR WATER GAS SHIFT REACTION, METHOD FOR REMOVING CARBON MONOXIDE IN HYDROGEN GAS AND FUEL CELL GENERATION SYSTEM

上記発明の明細書は、

☐ 本書に添付されています。

☐ ___月___日に提出され、米国出願番号または特許協定条約国際出願番号を________とし、（該当する場合）________に訂正されました。

the specification of which

☐ is attached hereto.

☒ was filed on March 16, 2000 as United States Application Number or PCT International Application Number PCT/JP00/01600 and was amended on ________ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration
(日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)
外国での先行出願

(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願年月日)	Priority Claimed 優先権主張 Yes はい	No いいえ
11-073270	Japan	18/03/1999	☒	☐
11-194104	Japan	08/07/1999	☒	☐

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.) (出願番号)	(Filing Date) (出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条 (c) に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Application No.) (出願番号)	(Filing Date) (出願日)	(Status: Patented, Pending, Abandoned) (現況：特許許可済、係属中、放棄済)

私は、私自信の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じるところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration
(日本語宣言書)

委任状：私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。
（弁護士、または代理人の指名及び登録番号を明記のこと）

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Japanese Language Declaration
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住所	Residence
国籍	Citizenship
郵便の宛先	Post Office Address

（第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。）

(Supply similar information and signature for third and subsequent joint inventors.)